

# An accurate temperature-controlled polarimeter

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*A photoelectric polarimeter has been constructed for the purposes of calibrating polarimetric standards and for re-determining the value for the specific rotation of sucrose in solution. The polarimeter has full circle rotation capability with sensitivity of 0.6 arc-sec (3  $\mu$ rad) and in specific measurements an estimated accuracy of  $\pm 2$  arc-sec at the 99% confidence level. The polarimeter uses both arc lamp and laser sources. Sample temperatures can be controlled to within  $\pm 0.5$  mK per day at, or around, 20°C, and six liquid, solid or gaseous samples may be simultaneously housed. Measurements of all six samples may be completed in a few minutes. In this paper we present the design details of this polarimetric system. The design required the careful application of high precision manufacturing techniques coupled closely with metrology throughout the manufacturing process.*

**Keywords:** Polarimetry, Standards, Calibration

Part of the mission of the National Bureau of Standards (NBS) is to provide accurate standards for national and international commerce. Many of these standards serve to define a common ground for analyses performed by buyer and seller. For instance, NBS issues a wide variety of Standard Reference Materials which are used to calibrate the measurement apparatus in the market-place. In order to provide these materials and other measurement services, NBS must build and maintain expertise and equipment in order to analyse and certify properties of reference standards to an accuracy which well exceeds the capabilities of the normal industrial or commercial research laboratory.

Three years ago, as a direct result of the need for a reliable and accurate reference point for the analysis of raw sugars and sugar products, we started a program to redetermine the 100 degree point of the saccharimeter scale. As an essential element of this program we had to construct a state-of-the-art polarimeter. This polarimetric system had to meet rigid requirements in order to assure the accuracy of the final measurements. In this paper we describe this apparatus in detail.

## General considerations

The 100 degree point of the saccharimeter scale is defined as the optical rotation of an aqueous solution containing 26.0160 g of pure sucrose per 100.00 cm<sup>3</sup>, measured at 20.00°C in an optical cell 200 mm long at a vacuum wavelength of 546.2271 nm<sup>1</sup>. A secondary definition in terms of the optical rotation of crystalline quartz allows the use of quartz plates as artefact standards<sup>2</sup>. Our efforts were directed towards realizing the primary definition, although, for historical reasons, any apparatus we constructed also had to be capable of measuring the quartz artefact standards.

The preceding definition is deceptively simple. Difficulties arise when one attempts to realize it to high accuracy. Our design goal was  $\pm 1$  arc-sec (5  $\mu$ rad). Since the

100 degree point of the saccharimeter scale corresponds to an optical rotation of about 40 arc-deg, this design goal translates to about  $\pm 6$  ppm<sup>†</sup>. The barriers to obtaining this accuracy are best understood by examining the coefficients listed in Table 1. Shown here are the uncertainties in the contributing physical parameters that would lead to a  $\pm 1$  arc-sec uncertainty in the optical rotation of a normal sucrose solution and a standard quartz plate. Note that the measured rotation is a function of the source wavelength, the optical path length, the cell window birefringence, the sample temperature, the ambient magnetic field, the light collimation and the optical alignment as well as the sucrose concentration. Furthermore, the definition is based on a concentration that cannot be accurately prepared experimentally. The volume of solution is defined, not the mass. Because of the practical impossibility of preparing a solution by volume to an accuracy of a few parts per million, one can only approximate the definition. The experiment can be done by preparing solutions that bracket the defined concentration, then least-squares fitting the measured optical rotations as a function of concentration and interpolating to the specific rotation at the defined concentration. In order that this procedure does not degrade the experimental accuracy, many solutions must be measured, each subject to the constraints shown in Table 1.

The accuracy requirement also constrains the measurement method to some extent. For true measurement assurance, one must not only take into account the historical record<sup>3</sup> but also provide, within the experimental design, constant cross-checks that ensure the correct functioning of the measuring instrument<sup>4</sup>.

## Description of the instrument

With the above constraints in mind, we constructed the apparatus shown in Fig 1. For the purposes of explanation, we have divided the device into three functional blocks: the sample enclosure, the polarimeter and the optical light sources.

## Sample enclosure and sample cells

The sample enclosure was designed to house six sample cells to maintain them in an isothermal and a low magnetic environment, and to allow them to be inserted into the measurement path while maintaining the optical alignment. The cells themselves determine the sample length and maintain the solution purity.

Each of the six cells for containing sugar solutions is a cylinder, machined from high conductivity copper. They were ground to nominal 38 mm od x 15 mm id within  $\pm 0.005$  mm. The ends of each cylinder were ground perpendicular to the outside surface and then lapped flat. The cells were rhodium plated to prevent corrosion.

<sup>†</sup>The degree on the saccharimeter scale is not equal to a degree of arc for historical reasons. Throughout the rest of this paper, we will use the degree of arc exclusively and will no longer refer to the saccharimetry degree

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The size of each cell was carefully measured during and after manufacture. The flatness was measured using a Zeiss<sup>19</sup> Kösters interferometer<sup>5</sup>. The parallelism of the end faces was measured using two autocollimators<sup>6</sup>. The cells were set in a precision V-block, and the deviation from face perpendicularity was measured at four rotational positions 90° apart. The length of the cells was measured by wringing a known gauge block to each face comparing the resultant length against NBS master gauge blocks in a mechanical comparator<sup>7</sup> which was refitted with a fringe counting laser interferometer. The "slave" blocks were used to eliminate the unknown surface deformation of the rhodium-plated copper. As a cross-check, the cells were remeasured using a bench micrometer set with master gauge blocks. In Table 2, we summarize these measurements on the completed cells at a temperature of 20°C. The face perpendicularity numbers are for the largest deviation observed.

To utilize the mechanical precision of the cell to control the optical path length, the windows are attached to the cell faces by a partial wring. A copper retainer is used to maintain the window position. Uniform pressure and gap distance between the cell face and the inner window surface are measured by observing white light interference fringes. The windows are low strain Homosil<sup>19</sup> (birefringence 1 nm/cm) finished to ¼ wave flatness and 1 arc-sec parallelism at NBS.

Two 12 mm diameter threaded wells are provided in each cell to facilitate filling with solution. The solution enters the bore of the cell through a 3 mm diameter hole in the bottom of one of the wells. Air bubbles are pushed into and trapped in the other well which is connected to the bore of the cell by a 1 mm diameter hole. The surface tension prevents the bubble from entering the optical path when the cell is rotated. Both wells are sealed with gold-plated brass plugs and O-rings. The plug for the air trap has a cavity to contain the air bubble. The air bubble permits thermal expansion of the solution.

Similar cylindrical cells were fabricated to hold quartz plates. The ends were not lapped; instead, the bore was enlarged and threaded to accommodate mounts typically used for quartz control plates<sup>8</sup>.

Six cells can be inserted at one time into the environmental chamber. This chamber and a sugar solution cell are schematically shown in Fig 2.

The chamber is a six-layered cylindrical thermostat. An aluminium inner core holds the cells and rotates with respect to the total housing. It is surrounded by an aluminium heater shell, a bakelite insulation shell, a copper cooling shell, a second bakelite insulating shell and a final mu-metal ambient temperature shell which also provides magnetic shielding. The mu-metal shell, not shown in Fig 2, fits snugly around the whole chamber.

The cells are slide fit into the inner core, which is

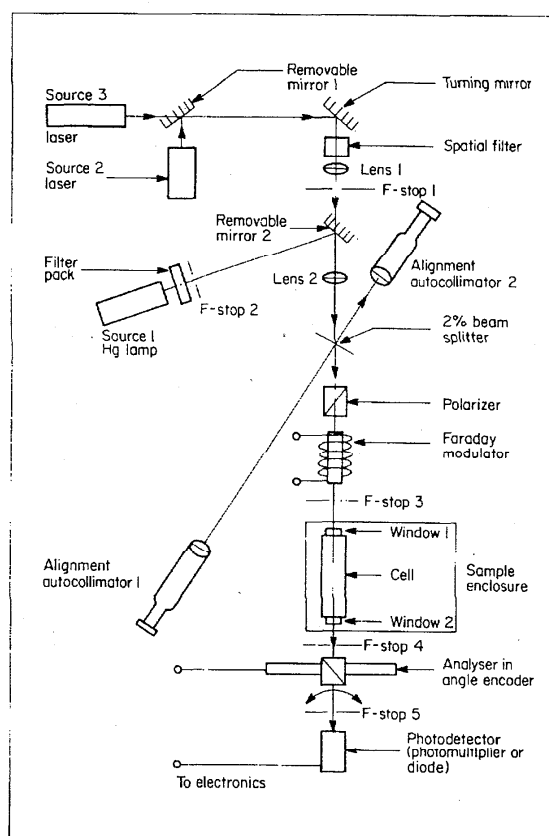


Fig 1 Photoelectric polarimeter

Table 1 Factors affecting the measured rotation

Parameter	Nominal Value	Magnitude of change causing 1 sec rotation error	
		24% sucrose (200 mm)	Quartz (50 mm)
1. Source wavelength	546 nm	$1.6 \times 10^{-3}$ nm	$5 \times 10^{-5}$ nm
2. Sample temperature, °C	20	0.015	0.0015
3. Sample alignment <sup>a</sup> , minutes	0	20	4
4. Magnetic field, gauss	0	0.06	0.20
5. Optical path length	See Table 2	1.3 $\mu$ m	11 nm
6. Cell window parallelism <sup>a</sup> , sec	0	30	—
7. Crystal face parallelism <sup>a</sup> , sec	0	—	0.25
8. Beam divergence <sup>a</sup> , minutes	0	20	4
9. Sucrose concentration, wt%	24	$10^{-4}$	—
10. Window birefringence <sup>b</sup> , deg	0	0.18	—

<sup>a</sup>Computed value assumes all light travels on the trajectory of greatest effect and that other alignment parameters, items 3, 6, 7 or 8, are at their ideal values

<sup>b</sup>Computed value assumes an ideal polarimeter and uses a first order approximation. The actual situation is now being studied

Table 2 Cell measurement results

Cell number	Perpendicularity, sec		Parallelism, sec	Length, mm	Length uncertainty, $3\sigma$ (mm)
	Face A	Face B			
1	$18 \pm 1$	$19 \pm 1$	$1 \pm 1$	c	—
2	8	11	3	200.91090	$\pm 0.00011$
3	12	12	1	200.06046	0.00013
4	7	12	6	200.89277	0.00010
5	7	12	6	200.76533	0.00006
6	8	13	5	200.93310	0.00010

<sup>c</sup>Cell number 1 was damaged during plating and was not judged to be of sufficient quality for use

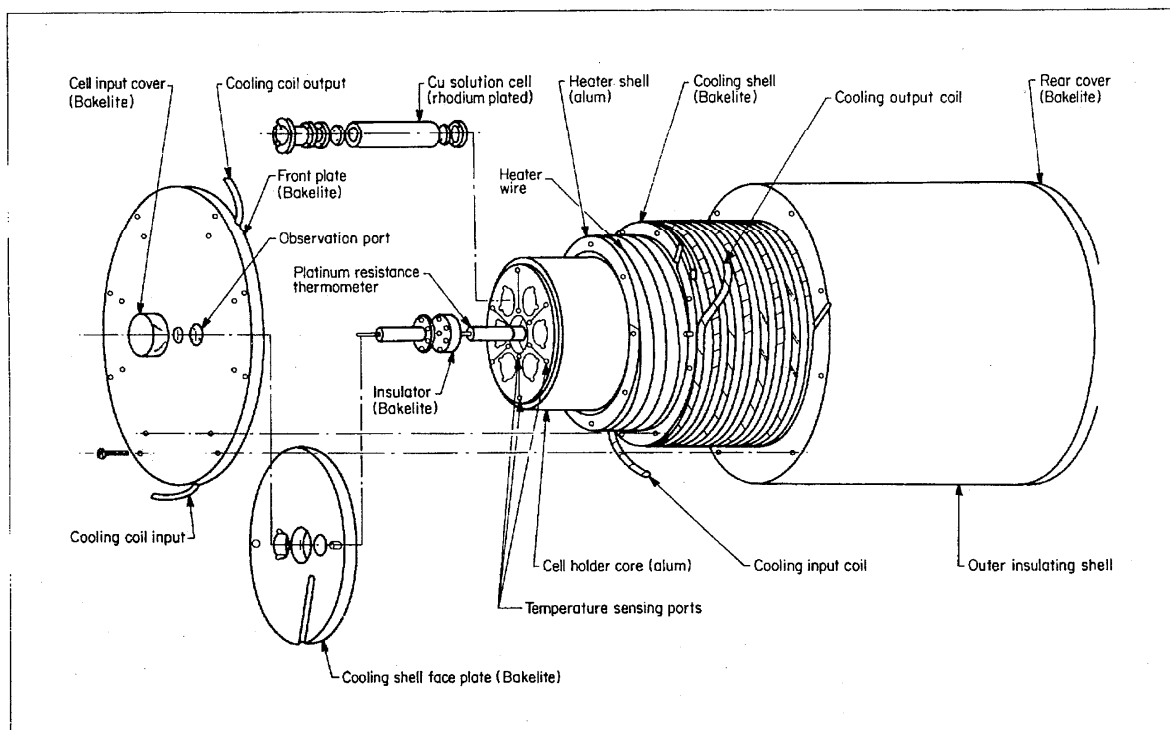


Fig 2 Sample enclosure and cell

mounted on class seven ball bearings to the heater shell. This core contains six bored holes 300 mm long which are parallel within  $\pm 40$  arc-sec and positioned so that each cell can be rotated into the light path. The cell can be removed when located at a position 180 arc-deg from the measuring position. The rotary position of the core is controlled by an external indexing lever. The lever drives a stainless steel tube mounted to the core by a bakelite stand-off which minimizes thermal coupling. The bearings reproduce the angular alignment of the cell (determined by the drum bore) with respect to the light path to within  $\pm 2$  arc-sec. This was measured by autocollimation of the cell windows with Autocollimator 1 which is a permanent part of the apparatus (see Fig 1).

The temperature control is accomplished in three stages. First the outer mu-metal shell is controlled by maintaining the ambient air temperature within  $\pm 0.2^\circ\text{C}$  in a special room designed for this purpose<sup>9</sup>. Next chilled water,  $0.2$  to  $0.6^\circ\text{C}$  ( $\pm 0.05^\circ\text{C}$ ) lower in temperature than the desired sample temperature, is circulated through copper tubing formed in a double spiral to make up the

cooling shell. The double spiral allows water to simultaneously enter and exit at the end of the unit. This eliminates a uniform temperature gradient. A commercial water bath circulator with on-off control is used for this task.

This cooling shell is separated from the heater shell by a 25 mm thick bakelite insulating shell. The aluminium heater shell has a bifilar heater wire ( $5\ \Omega/\text{m}$ ) wound around it in spiral grooves. A thermistor embedded in this shell senses the temperature, and the feedback circuit (see Fig 3) controls the heater voltage. dc circuitry is used to minimize cost.

The thermostat core, which holds the cells, is coupled to the heater shell by a 0.02 to 0.08 mm air layer and the bearings. Its temperature is monitored both by thermistors and a platinum resistance thermometer. Measurement sensitivity of  $\pm 0.01\ \text{mK}$  is accomplished using the thermistor and the ac bridge shown in Fig 4. The capsule platinum resistance thermometer calibrated at the NBS Temperature Section based on an International Practical Temperature Scale of 1968 provides a reference. Its resistance is measured with a calibrated Mueller Bridge. The temperatures

measured in the core are stable to better than  $\pm 0.001^\circ\text{C}$  short term and  $\pm 0.0005^\circ\text{C}$  over extended periods. We estimate our temperature accuracy to be  $\pm 0.001^\circ\text{C}$ .

### The polarimeter

The layout of the polarimeter proper is shown in Fig 1. The light from the source is first polarized by a schlieren-free Glan-Thompson prism. It then enters the Faraday Modulator (Hoya<sup>19</sup> Type FR-5 Glass) which modulates the plane of polarization  $\pm 1$  degree at 100 Hz. Both the polarizer and the modulator are slightly tilted with respect to the optic axis in order to prevent reflections from their surfaces and from reaching the analyser. (Coatings are not used because they often exhibit anisotropic behaviour.) The light next passes through the cell, with an F-stop before and after, and is incident upon the analyser, which is also a schlieren-free Glan-Thompson prism. The analyser is contained in a 21-bit optical encoder, and the null is detected by either a photomultiplier (RCA 7265)<sup>19</sup> or a photodiode (UDT PIN 10)<sup>19</sup> depending upon the source. Autocollimator 1 is used to check the alignment of the cell and analyser. A precalibrated retroreflector ( $\pm 1$  arc-sec) is used at F-stop 4 to provide this autocollimator with the beam reference direction.

Detailed discussions of the principles of the Faraday effect modulation scheme for polarimetric null detection are given in the literature<sup>10-12</sup>. For our purposes, it is sufficient to state that there exists an ac photo-current at the modulation frequency which changes phase by 180 deg at the polarimetric null. This enables one to use phase-sensitive detection techniques which allow working close to the theo-

retical signal-to-noise limitations. A block diagram of the electronics used is shown in Fig 5.

All optical components are aligned and centered 228.6 mm above the table surface on massive aluminium pedestals which are bolted to the nonmagnetic stainless steel surface of an optical bench. The polarized segment of the light path is perpendicular to the ambient magnetic field.

The azimuth of optical rotation is measured with an optical encoder (ITEK Digisec RI21/158(c)—QPZ)<sup>19</sup> with a

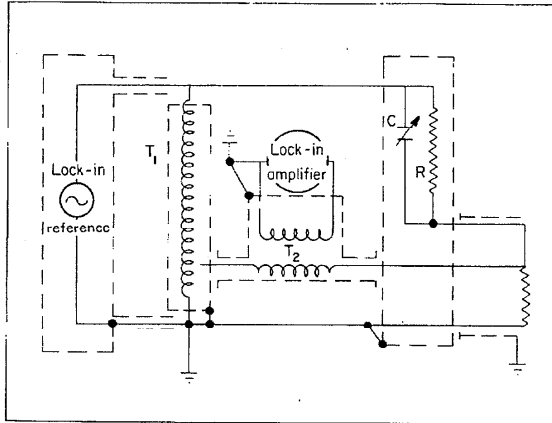


Fig 4 ac bridge circuit.  $T_1$  : 7 digit ratio standard,  $T_2$  : isolation transformer,  $C$  : precision capacitance standard and  $R$  : a  $2k\Omega$  low thermal coefficient resistor. Detector and source are combined in commercial lock-in amplifier

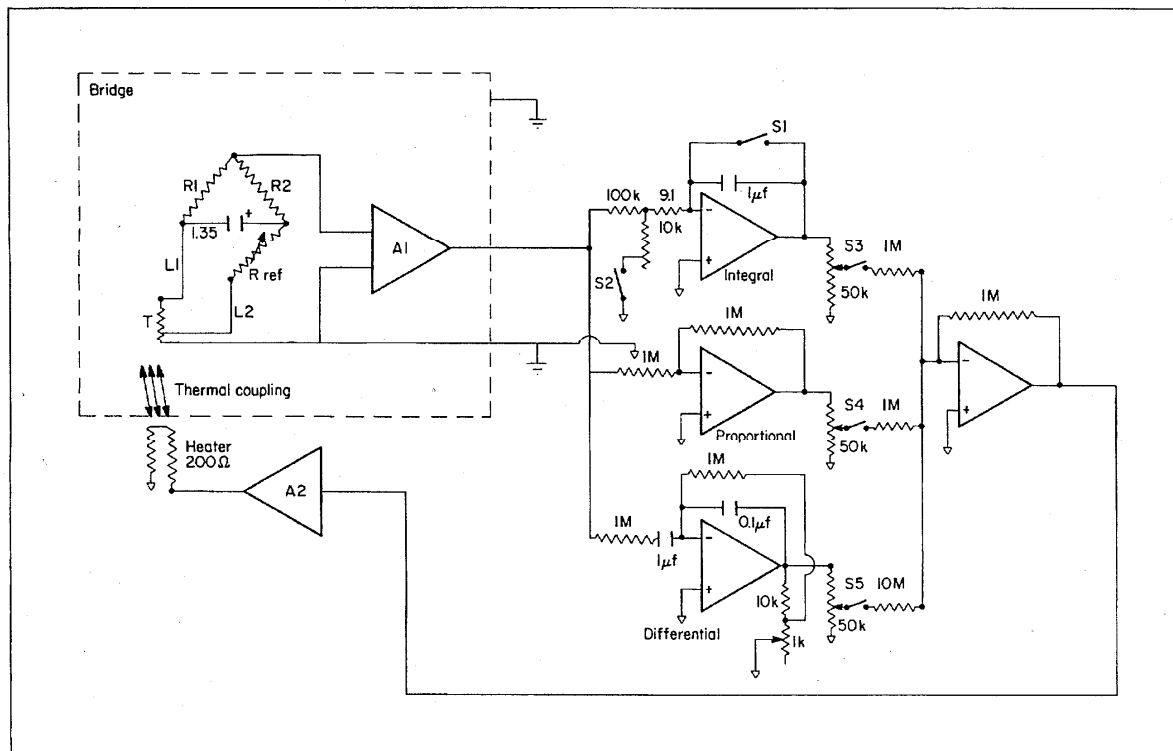


Fig 3 Heater shell temperature control cell. All operational amplifiers are LF 356. A1 is a microvoltmeter. A2 is commercial power supply. Integrator capacitor is polystyrene. S1 is normally open. S2–5 are normally closed except during tuning. L1 and L2 are matched leads. All control pots are ten turn wire wound. R1 and R2 are Vishay Resistors. T is a thermistor

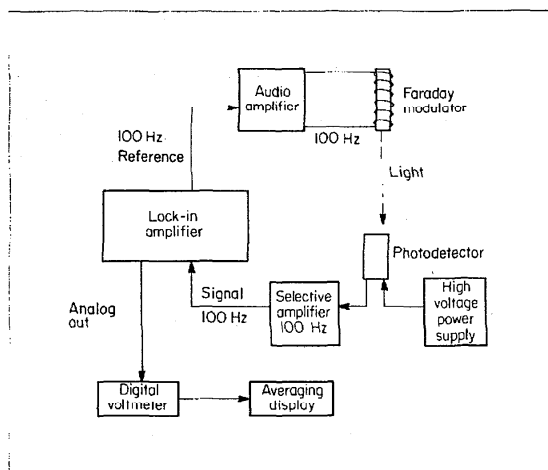


Fig 5 Polarimeter null-detection electronics

least significant count of about 0.6 arc-sec. This encoder was calibrated against an NBS indexing table accurate to  $\pm 0.1$  arc-sec that had been previously calibrated against another indexing table by sub-division<sup>13</sup>. The accuracy of the encoder was better than 1 bit as long as zero crossing was avoided. The calibration data are shown in Table 3 for a 60 deg increment.

The analyser is inserted in an adjustable mount in the centre of the encoder, and autocollimation is used to adjust the prism face perpendicular to the rotation axis to within  $\pm 1$  arc-sec.

The driving mechanism for the encoder is a modified sine bar arrangement using two stepping motors. The sine bar is connected at one end to a hollow shaft whose axis is coincident with the encoder axis. Attached to this arm is a stepping motor whose output shaft is a 22 mm diameter rotor fitted with two 0-rings. The motor position is adjusted such that a gentle but firm friction contact is maintained between the 0-rings and the encoder rotor. This motor provides coarse angle adjustment. At the end of the arm another motor is connected through a micrometer screw to provide the fine adjustment. (The holding torque of the coarse motor provides sufficient force for the sine bar to function.) Both stepping motors are rated at 200 steps per revolution. However, a sine/cosine driving circuit which subdivides each motor step into 31 equal parts is used<sup>14</sup>. The encoder therefore moves 26 arc-sec per step of the coarse position motor and 0.06 arc-sec per step of the fine adjustment. Maximum speeds are 502 deg/min and 1.14 deg/min respectively.

### The sources

The system uses both laser and conventional low-pressure mercury arc sources. The laser sources include unpolarized and polarized HeNe lasers, Lamb-dip stabilized and iodine absorption stabilized HeNe lasers, a HeCd laser, and a single-frequency dye laser locked to the desired wavelengths using the optogalvanic effect<sup>15</sup>. Because of their inherent collimation and spectral purity, the lasers require a minimum of optics. We have used these sources with or without the spatial filter shown in Fig 1. When using the spatial filter, Lens 2 is removed and Lens 1 ( $F = 100$  mm) provides the collimated beam. When removing the spatial filter, Lens 1 focuses the light at the focal point of Lens 2, which then provides

Table 3 Encoder calibration's values

Angular interval, deg	Deviation, sec
0-1	-0.02
0-2	0.20
0-3	-0.16
0-4	-0.12
0-5	-0.13
0-30	0.16
0-60	0.43

Table 4 Summary of polarimeter performance

Wavelength uncertainty (Hg lamp)	$\pm 0.003$ nm
Sample temperature	
Gradient	$< 10^{-3}$ °C
Drift	$< 5 \times 10^{-4}$ °C/day
Absolute	$\pm 0.003$ °C
Sample misalignment	$< 1.3$ minute
Magnetic field (Hall effect probe)	$< 5 \times 10^{-3}$ gauss
Cell-window parallelism	$< 6$ arc-sec
Analyser angle accuracy	$\pm 0.62$ arc-sec
Optical path length (sucrose cells)	$\pm 0.2$ $\mu$ m
Null point determination	
Mercury lamp, $\xi = 90$ arc-sec	$\pm 0.6$ arc-sec
Laser, $\xi \approx 1$ arc-sec	$\pm 0.6$ arc-sec
Maximum beam divergence	
Arc lamp	$< 14$ minute
Laser	$< 0.7$ minute
Window birefringence	
unmounted	$< 10$ nm/cm (1000 nm/m <sup>2</sup> )

the collimated beam. This latter set-up is most convenient when one intends to switch from laser to arc lamp sources.

The use of the arc lamp requires more care due to the low intensity of the source. We use a low pressure stabilized dc discharge in a Philips type 93123<sup>19</sup> mercury discharge lamp. The 546 nm emission is separated from the other mercury wavelengths with a prism monochromator followed by a special NBS filter pack. The filter's bandwidth at half maximum transmittance is 10 nm.

The collimation system is essentially the same as that described by Olson<sup>11</sup>. The light emerging from the filter pack passes through a 4 mm diameter pin hole F-stop at the focal point of the collimating lens. The collimating lens is followed by a field stop, 8 mm diameter, at a distance equal to the focal length of the lens. Other F-stops are used as shown in Fig 1. This system has a maximum divergence of  $4 \times 10^{-3}$  rad and a throughput of  $2.4 \times 10^{-5}$  cm<sup>2</sup> sr.

### Polarimeter performance

We have been using the polarimeter nearly continuously for the last two years for determining the optical rotations of sucrose solutions and quartz control plates. The results on the sucrose are reported elsewhere<sup>16,17</sup>. Two methods were used to determine the null of the instrument when using the mercury arc lamp: a) the method of Olson<sup>11</sup> where the lock-in output is averaged for ten seconds at each of five angular positions in a range of about 40 arc-sec straddling the null point; and b) averaging the lock-in output for 90 s at each of two angles, three arc seconds on either side of the null. The null angle is determined by

linear interpolation for both methods. Both methods yield reproducibility of  $\pm 0.6$  arc-sec (1 bit) but the former method has a sounder statistical basis. When using the laser sources, similar sensitivity was easily obtained by directly observing the lock-in analog output after a 0.3 s time constant filter.

The performance of the polarimeter is summarized in Table 4. All parameters have met or exceeded the design goals. Further, as a test of accuracy, we have compiled a history of measurements on quartz control plates. For example, our average rotation value,  $\alpha$ , for NBS plate 1724, is  $38.9219 \pm 0.0006$  deg with mercury lamp and filter pack and is in good agreement with the value of  $38.9218 \pm 0.0006$  deg obtained in previous international comparisons<sup>18</sup>.

The instrument is now being used routinely to measure quartz control plates and certify the Standard Reference Materials. Furthermore, the work is progressing towards a better definition of the standard by using laser sources and resolving some remaining questions regarding sucrose impurities and cell window birefringence.

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